**Heterogeneous Catalysis Using electron Beam Treated Catalysts**

Suresh B 1 and G. Vanmathi 2

1. Researxh Scholar, Department of Chemistry, Kamaraj College, Tuticorin

2. Assoc Prof., Department of Chemistry, Kamaraj College, Tuticorin

Organic synthesis has grown wider enough seeking selectivity and efficiency in organic transformations. With the fast growth in Pharmaceutical Chemistry, new drug discovery is looking for effecting conversions with high stereoselectivity and high regioselectivity. Such conversions need to be essentially Green chemistry approach, which is also called as sustainable chemistry, as the earth can no longer continue to tolerate high polluting streams, and environmental hazards. Scientists all over the world are looking for cost-effective reactions, which affords high yield and high quality. Economics, Environment, Safety, Quality and high throughput are the demanding requirements of today. Heterogeneous catalysts are the choice to achieve most of these requirements, as they are reusable for several cycles, and do not get consumed in reactions, unlike homogeneous catalysts. Unlike other reagents, catalysts do not generate effluents by themselves, & provide high atom efficiency. However, question of selectivity or specificity remains to be still an area of opportunity for Organic Chemists.

Catalysis is the process in which the rate of a chemical reaction is either increased or decreased by means of a chemical substance known as a catalyst. The general feature of catalysis is that the catalytic reaction has a lower rate-limiting free energy change to the transition state than the corresponding un catalyzed reaction, resulting in a larger reaction rate at lower temperature. However, the mechanistic origin of catalysis is complex.

Effectiveness of heterogeneous catalysis relies on the micro surface nature of the solid phase on to which both the reagent and the starting material get adsorbed prior to the reaction. Uniformity of the surface also plays a major role in effecting selectivity or specificity. If one were able to treat the solid surface appropriately, it is possible to control the progress and path of the reaction in such a manner to achieve the desired molecular conversion, as the very reaction primarily depends on the micro structural features of the solid surface. Electron Beam Treatment of the solid phase of heterogeneous catalysts could be one such option, but not a well-studied area to effecting selective organic transformations. We are interested in evaluating the influence of Electron Beam from the Microtron on certain heterogeneous catalysts and how they would get ultimately translated into the functional group conversions. In a broad study, we would conduct experiments to understand the consequence of microtron treatment of heterogeneous catalyst on the deprotection of aryl methyl esters of carboxylic acids containing competing functional groups for the catalysts. Such study would open up new life for this kind of Chemistry, and help medicinal chemists to explore this area of research to induct in to the regular synthesis.

The catalytic power of the catalysts depends upon their surface activity. Modification of the surface can improve the catalytic activity. Recently, researchers are looking for methods to enhance the surface activities of the catalyst. Few reports indicate that irradiation by electromagnetic radiations like γ – rays and radiofrequency. For instance, the effect of electron irradiation on the properties of the systems 1% Pd/C, 1% Pd/Al2O3, and 1% Pd/TiO2 is studied in gas-phase and liquid-phase toluene hydrogenation. An increase in the irradiation dose to 120-900 Mrad increases the catalytic activity by a factor of 2-8 relative to that of the original system. XPS data for the Pd/C catalyst suggest that, after irradiation with high-energy electrons, the metal particles are stabilized on the surface of the carbon support, their degree of dispersion is increased, and their sintering is suppressed. These inferences are consistent with the observed changes in catalytic properties. Further, CuO–Al2O3 samples containing different amounts of copper oxide were γ-irradiated with 10, 25, 50 or 90 M rad. It has been found that the catalytic parameters of the samples investigated are influenced strongly by the metal loading and γ-irradiation dose.

As a part of our investigation of Organic Reduction reactions using **Electron Beam Treated** heterogeneous catalysts we conducted experiments to understand the consequence of microtron treatment of heterogeneous catalyst on the deprotection of aryl methyl esters of carboxylic acids containing competing functional groups for the catalysts***.*** When the catalyst is exposed to a high-energy electron beam, the combined physical and chemical effect of accelerated electrons can produce new types of active sites with unusual and valuable catalytic properties, such as enhanced activity and stability [3-6]. Such study would open up new life for this kind of chemistry, and help medicinal chemists to explore this area of research to induct into the regular synthesis.

Nano particles of metals have excellent catalytic ability and they find wide applications in synthetic organic chemistry. Such environment friendly green reactions can produce higher yields with less waste.

In this proposed work **metal / nano metal particles** on **carbon/metal oxide** support (with and without Electron Beam Treatment) for the synthesis of various organic compounds. Heterogeneous catalysis has supreme importance in many areas of the chemical and energy industries. Palladium catalyzed reactions and hydrogenation reactions have gained enormous importance in modern organic synthesis as the coupling products obtained via these reactions have been applied as intermediates in the synthesis of several functional materials, natural products, and bioactive compounds. Such catalysis occurs primarily at certain favourable locations on the surface, called active sites [1, 2].

Palladium catalysts have been developed for the selective, mild amination of nitro aryl compounds. In this study aromatic nitro compound viz., 2-iodo nitrobenzene was reduced by 10% Pd/C (50% wet) to 2-iodo aniline.



**Figure 1.Amination of Aryl Nitro compound**

 A solution of 2-iodo-nitrobenzene (2 g) in methanol (40 mL) and 10% Pd/C (0.3 g; 50% wet) were charged into a Parr hydrogenator vessel and flushed with nitrogen. Hydrogen was passed into the vessel at a pressure of 5 atm and temperature of 26-28 0C. The course of the reaction was monitored by TLC using a mixture of heptane and ethyl acetate (7:3) as mobile phase and silica gel coated alumina plate as Stationary Phase. The Product 2-iodoaniline was obtained in pure form. The reactions were conducted under similar conditions using 150 kGy, 200 kGy, 250 kGy irradiated 10% Pd/C samples. The results showed that the reaction time decreased progressively upon employing irradiated catalysts. The time for reduction with 250 kGy irradiated catalyst is half that of non irradiated catalyst (7 – 9)

**Table 1. Reduction of 2-iodonitrobenzene to 2-iodoaniline**

Wt. of 2- iodo nitrobenzene taken = 2 g

|  |  |
| --- | --- |
| **Electron beam dosage on 10% Pd/C ( kGy)** | **Time for reduction of reactants (h)** |
| 0 | 10 |
| 150 | 7 |
| 200 | 6 |
| 250 | 5 |

The formation of the product, 2-iodo aniline was confirmed by FT-IR, NMR and Mass spectra. The surface area of Pd/C catalysts, both irradiated and non-irradiated was measured by using low pressure N2 BET surface Analyzer. BET surface area and Langmuir surface area are reported in Table 2. Both BET and Langmuir surface area were found to increase upon irradiation, 572.95 m2/g to 807.91 m2/g & 862.86 m2/g to 1200.40 m2/g respectively. This revealed the dispersion of palladium and increase in number of active sites.

**Table 2. Surface Area of Pd/C**

|  |  |  |
| --- | --- | --- |
| **Catalyst** | **BET surface area (m2/g)** | **Langmuir surface area (m2/g)** |
|  Pd/C Non irradiation | 572.95 | 862.86 |
|  Pd/C 150 kGy irradiation | 621.11 | 939.87 |
|  Pd/C 200 kGy irradiation | 743.19 | 1104.90 |
|  Pd/C 250 kGy irradiation | 807.91 | 1200.40 |

**Cyclic voltammetric studies**

The cyclic voltammetric studies of all 10% Pd/C samples were undertaken at a given potential of 0.1 V Vs SCE (Fig 2 – 5) using CH Instruments, USA.

 **Cyclic Voltammograms of 10% Pd/C**

Nonirrad Pd/C

Fig. 2

150 kGy

Pd/C

Fig.3

200 kGy Pd/C

Fig.4

250 kGy Pd/C

Fig.5

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Electrochemical surface area calculated from the cyclic voltammetric studies[7, 8] revealed the increase in surface area of the irradiated Pd/C catalysts as given in Table 3. The Pd atoms on the surface of the catalyst was found to increase in the relative order of 250 kGy > 200 kGy > 150 kGy > Nonirradiated Pd/C.

Electrochemical surface area and number of active Pd atoms on the surface were calculated as, Electrochemical surface area = Q / 240µC cm2

No. of active Pd atoms on the surface = Electrochemical Surface area in cm2× 1.5×1015)

**Table. 3 Electrochemical surface area**

|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | **Charge (µC)** | **Electroche.surface area (cm2)** | **No. of active Pd atoms on the surface** |
| Pd/C | Negligible | **-** | **-** |
| Pd/C 150 kGy | 179.0 | 0.745 | 1.117×1015 |
| Pd/C 200 kGy | 190.62 | 0.801 | 1.201×1015 |
| Pd/C 250 kGy | 246.8 | 1.028 | 1.542×1015 |

The reduction reaction using various electron beam treated Pd/C catalysts have shown enhanced catalytic activity. When the reaction is repeated with the same irradiated catalyst after a period of 3, 6 and 9 months, the product yield and reaction time for hydrogenation were found to be maintained as that of freshly irradiated catalysts. The efficiency remained unaltered at least for one year. The reduction time decreased by 15 -70% with the electron beam irradiated catalyst. The reduction was complete in the following order of dosages 250 kGy > 200 kGy >150 kGy > non irradiated Pd/C. Further the SEM–EDX and metallurgical microscope reports of Pd/C confirmed the increase in dispersion of Pd particles [9]. The electron beam irradiation of Pd/C has enhanced the catalytic activity in terms of yield and reduction process. This is a promising result for industrial application involving Pd/C as catalyst in manufacturing process.

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